8-1956

Caustic fusion of columbite-tantalite concentrates with subsequent separation of niobium and tantalum

J. A. Pierret
Iowa State College

H. A. Wilhelm
Iowa State College

Caustic fusion of columbite-tantalite concentrates with subsequent separation of niobium and tantalum

Abstract
A procedure for the production of spectrographically pure niobium and tantalum oxides from columbite-tantalite concentrates was developed in this study. The procedure involves a caustic fusion process and the separation of tantalum and niobium by liquid-liquid extraction.

Disciplines
Chemistry

UNCLASSIFIED

UNITED STATES ATOMIC ENERGY COMMISSION

ISC-796

CAUSTIC FUSION OF COLUMBITE-TANTALITE CONCENTRATES WITH SUBSEQUENT SEPARATION OF NIOBIUM AND TANTALUM

by

J. A. Pierret and H. A. Wilhelm

August 1956

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

UNCLASSIFIED

This report is distributed according to the category Chemistry - General, as listed in TID-4500, January 15, 1957.

Printed in USA. Price 25 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

CAUSTIC FUSION OF COLUMBITE-TANTALITE CONCENTRATES WITH SUBSEQUENT SEPARATION OF NIOBIUM AND TANTALUM*

by

James A. Pierret and Harley A. Wilhelm

ABSTRACT

A procedure for the production of spectrographically pure niobium and tantalum oxides from columbite-tantalite concentrates was developed in this study. The procedure involves a caustic fusion process and the separation of tantalum and niobium by liquid-liquid extraction.

The finely ground ore is fused with sodium hydroxide. The fused material is cooled and washed with cold water to remove most of the tin, silicon, and aluminum and part of the manganese. The reddish residue is made into a thick slurry by adding a small amount of water and stirring. Diluted sulfuric acid (1:1) and iron powder are added to aid in dissolving the manganese; then more water is added to bring the sulfuric acid to about 1 molar. The insoluble residue which contains the niobic and tantalic acids is recovered by filtration. It is washed and then dried at about 200 degrees Centigrade.

The dried residue which contains 5-10 per cent impurities is dissolved in a minimum amount of 70 per cent hydrofluoric acid. Tantalum and niobium are extracted from the aqueous hydrofluoric acid solution by the addition of an immiscible organic solvent, leaving most of the impurities in the aqueous phase. By washing the separated organic with portions of a dilute sulfuric acid solution, niobium with a small percentage of tantalum is removed from the organic. A small amount of niobium then remains in the tantalum-rich organic phase. Pure niobium oxide was obtained

---

*This report is based on an M.S. thesis by James A. Pierret, submitted August, 1956, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

by combining all of these aqueous washes and extracting with fresh organic solvent to remove the small percentage of tantalum. Pure tantalum oxide was obtained by adding some hydrofluoric acid to the tantalum-rich organic phase and extracting with additional dilute sulfuric acid to remove the residual niobium.

A comparison of tributyl phosphate-dibutyl ether solution and methyl isobutyl ketone (hexone) as the organic solvent for the extraction is given. The hexone extracted more niobium but less tantalum from the hydrofluoric acid solution of the dried residue, but the analytical data indicated a better separation of niobium from tantalum with the tributyl phosphate solution.

I. INTRODUCTION

At the present time there is an increasing interest in tantalum and niobium metals. The chief commercial use of tantalum has been for the construction of acid-proof equipment for the chemical industries. Because of the unique nature of tantalum metal it is being used extensively in the construction of electronic equipment. Tantalum is also receiving consideration as a material of construction for containers of certain liquid fuels in nuclear reactors. Niobium, which has a relatively low capture for slow neutrons (1), is also highly refractory and corrosion resistant. Niobium and its alloys are being investigated as possible materials for use in nuclear reactors and in equipment requiring materials with high temperature strength and corrosion resistance. The present costs of both pure tantalum and niobium as oxides or as finished metals are many times the costs of these elements in their ore concentrates. There is an increasing need for improved, more economical ore treatment and purification processes for these elements because of the expanding interest in their potential applications. This report presents results of a study of certain chemical treatments of columbite-tantalite ore concentrates and results of an investigation of a method for subsequent separation of the two elements to obtain their purified oxides.

The nature of tantalum and niobium and of their compounds has long perplexed many investigators. The coexistence of both elements in minerals and their chemical similarities caused confusion in connection with their discovery. These two elements occur in lean deposits that are widely scattered throughout the world. They present unique processing problems to obtain their purified oxides from ores. These problems arise from the fact that niobium and tantalum are always found together in a variety of minerals that are relatively insoluble and that they are chemically quite similar and form only a few highly soluble compounds. For many years the only commercial process for separating niobium and tantalum has been based on a slow fractional crystallization of their double fluorides with potassium.

In connection with the work reported here, a two-part laboratory procedure was developed for obtaining niobium and tantalum pentoxides from columbite-tantalite ore concentrates. In the first part the ore is opened by a

caustic fusion and some of the impurities are removed by washing with water and then with diluted sulfuric acid. In the second part, batch liquid-liquid extraction is applied to a hydrofluoric acid solution for the purification and separation of fluoniobic and fluotantalic acids, which can be readily converted to the oxides. Only a few stages of a countercurrent extraction should be required for the efficient separation of these oxides. A combination of both treatments should be suitable for low-cost, quantity production of the pure oxides from their ore concentrates.

II. REVIEW OF LITERATURE

A. Opening of Niobium and Tantalum Ores

Niobium and tantalum were first discovered in 1801 by Hatchett in a Connecticut mineral (2). These elements rarely exist in a free state and occur generally as negative radicals in many minerals in which the oxides of iron, manganese, calcium, and various rare earths form the bases. The chief source of the elements are the minerals columbite and tantalite, but some of the other important minerals are samarskite, pyrochlore, yttrotantalite, fergusonite and wholerite.

In this study, work was confined to columbites and tantalites which can be formulated $Fe(Mn)(NbO_3)_2$ and $Fe(Mn)(TaO_3)_2$. When niobium predominates, the mineral is called columbite and when tantalum predominates, tantalite. Along with the variable amounts of iron and manganese, the chief impurities are silicon, tin, aluminum, titanium and tungsten. In the past many methods have been attempted for opening the ores and the chemical separation of the impurities. Some methods were better for removing certain impurities and others were better for removing other impurities. As a result the work was tedious and complicated, and quantitative procedures have depended greatly on the particular ore being treated.

The insolubility of tantalum and niobium compounds generally has led to a fusion process using a variety of salts, followed by leaching with water to remove some soluble impurities, and then an acid leach to give a purified mixture of the hydrated oxides of niobium and tantalum.

A common procedure of the early investigators was to fuse the finely ground powdered mineral with three to eight times its weight of potassium bisulfate. The cold, fused mass was digested with water which precipitated the hydrated oxides. Berzelius (3) washed the hydrated oxide residue with boiling water and after drying and calcining, heated it with a mixture of sulfuric acid and hydrofluoric acid to drive off the silica. This residue was digested for several days with ammonium bisulfide to remove stannic and tungstic oxides and to convert the iron to sulfide which in turn was removed with hydrochloric acid.

Others (4) removed silica by fusing the hydrated oxide residue from the bisulfate fusion with sodium hydroxide and washing then with water. Rather than using the ammonium bisulfate treatment, Rose (5) recommended that the hydrated oxide residue be fused with three times its weight of sodium carbonate and some sulfur. This product, after cooling, was washed with water and then with hydrochloric acid. Simpson (6) also fused tantalite with potassium bisulfate. He then immersed the cold, fused mass in dilute hydrochloric acid and boiled the solution until a white precipitate formed. The precipitate contained some silicon, tin, and tungsten.

Gibbs (7) employed a solution of potassium bifluoride to which he added powdered columbite and then evaporated the solution to dryness. This residue was treated with hot water and hydrofluoric acid. On cooling, plate-like crystals of potassium oxyfluoniobate, K_2NbOF_5, separated out and by recrystallization were freed of iron and manganese. He reported that this procedure was particularly useful when the titanium content was high.

Giles (8) recommended fusion with potassium carbonate. He mixed the powdered mineral with potassium carbonate and heated the mixture in a charcoal-reduced atmosphere. Because of the action of reducing gases the fused mass contained such metals as copper and tin and lower oxides of such elements as iron and manganese. The potassium compounds of tantalum and niobium in the fused mass were leached out with water.

Joly (9) heated powdered tantalite with a mixture of dry sodium carbonate and sugar charcoal for five to six hours in a graphite crucible at a high temperature. The

tantalum, niobium, and titanium were converted to carbides and nitrides. The product was digested with boiling concentrated hydrochloric acid until dry. The dried residue was heated in a current of chlorine and treated with hydrochloric acid again. The hydrochloric acid solution was diluted with water to precipitate the mixed oxides.

Hahn and Franke (10) opened the ores by heating them at 250-300 degrees Centigrade with carbon tetrachloride and extracting the product with acid.

Sears (11) opened columbite and tantalite ores by fusion with seven grams of sodium pyrosulfate per gram of ore. The fused product was disintegrated by soaking in water and washed by decantation with hot, 3 normal hydrochloric acid until free from iron. He studied the fusion over the range of 770-900 degrees Centigrade and the results indicated that variations in the proportion of flux and time of heating had little influence on the solubility of the product. He was able to obtain a complete separation of niobium and tantalum when the fusion was carried out at 835-870 degrees Centigrade. He heated the fused residue on a sand bath with sulfuric acid until boiling ceased. The niobium dissolved.

Rohiner (12) heated niobium and tantalum minerals with potassium hydrosulfate and sulfuric acid. The resulting mixture was then cooled, added to water, and boiled. The precipitate was washed and heated with hydrogen peroxide. Titanium was precipitated with sulfur dioxide.

Bhattacharya (13) states that Jhaijha columbite yielded pure tantalum pentoxide and niobium pentoxide after a potassium hydrosulfate fusion and a potassium carbonate fusion, followed by the extraction with water, and the precipitation of sodium tantalate and niobate by sodium chloride.

Balke (14) fused the finely divided ore with caustic soda to give iron and sodium salts. The fused product was washed with water and the residue treated with hydrochloric acid in order to remove the iron. The white crude tantalic and niobic acid remained. With a few refinements, this process is used for commercial production by Fansteel Metallurgical Corporation (15). Ore, chiefly tantalite, is passed through a jaw crusher and pulverized in a hammer

mill equipped with tungsten carbide tipped hammers. The pulverized concentrate is then fused with sodium hydroxide in a continuous fusion furnace at 1800 degrees Fahrenheit. The cooled fusion product is treated with hot water and steam to remove water-soluble materials and then leached with hot, dilute hydrochloric acid to give a white mixture of tantalic and niobic acid.

In a report of work done at the University of Nevada (16) columbite and tantalite ores were fused with 25-30 parts by weight of a flux consisting of two parts sodium peroxide and one part of sodium carbonate. All ores tested were easily decomposed. All of the more basic constituents such as titanium, manganese, iron, etc., were then soluble in hydrochloric acid while tantalum, niobium, and tungsten were insoluble. Digestion with ammonium hydroxide removed any remaining tungsten without affecting the solubility of tantalum and niobium.

Oka and Miyamota (17) decomposed columbite with a mixture of four parts sodium hydroxide to one part sodium peroxide. One part of ore was heated with 2.5 parts of this mixture to obtain decomposition. Tungsten was removed by filtering. Tantalum and niobium salts were dissolved in hydrogen peroxide.

Meyers and Greenwood (18) mixed one part of ore to three parts of a mixture consisting of sodium hydroxide and sodium carbonate in the ratio of nine to one. The fusion was followed by extracting with water and leaching with hydrochloric acid, which is a process quite similar to the Balke method.

A few investigators have tried opening ore without involving a fusion step. Fink and Jenness (19) applied a leaching process using fluorspar, concentrated sulfuric acid, oxalic acid, and steam. Fowler (20) roasted ores at 600-800 degrees Centigrade and digested at 200-400 degrees Centigrade with concentrated sulfuric acid and potassium sulfate. The soluble salts were removed by a water leach. The insoluble portion was dissolved in a solution of oxalic acid and potassium oxalate with the pH adjusted to two to three with hydrochloric acid.

Jenness (21) obtained tantalum and niobium from ore by chloridizing each metallic element in the ore and raising the temperature to the volatilization point of each chloride. Cavelliez (22) reported that niobium was separated from tantalum by roasting ore in air at 800-1200 degrees Centigrade with a basic substance which was usually calcium oxide. The residue from this roasting process was heated in a chlorine atmosphere at 800-1050 degrees Centigrade for several hours. Under these conditions 70-80 per cent of niobium was volatilized, practically all of the tantalum remaining in the mixture.

Earlier work at this Laboratory was done on the fusion of columbite-tantalite ore (23). Many fusion mixtures involving various reagents were studied; the most suitable method found for treating these ore concentrates was essentially a sodium hydroxide fusion. For general experimental purposes a standard procedure was set up for opening these ores. In this treatment a mixture of eight parts sodium hydroxide, four parts sodium peroxide, and ten parts of an ore was fused at a temperature of about 650 degrees Centigrade for 30 minutes. The fused product was leached with sodium hydroxide solution and with either hydrochloric acid or nitric acid to give a mixture of the insoluble acids of niobium and tantalum, which could be converted to the oxides by calcining. Although this earlier work gave oxides nearly free of impurities, the sodium peroxide and the acids used added costs that were somewhat unfavorable for large scale commercial production.

B. Separation of Tantalum and Niobium

The actual separation of tantalum and niobium generally has been accomplished after almost all of the impurities have been removed and a chemically purified residue of both niobic and tantalic acids has been obtained. Commercially the separation is done by fractional crystallization (15). The niobic and tantalic acids are treated with hydrofluoric acid and the resulting solution is saturated with potassium fluoride. Potassium fluotantalate crystallizes out leaving niobium in solution. After further evaporation potassium oxyfluoniobate is precipitated.

Work in this Laboratory on liquid-liquid extraction for the separation of tantalum and niobium was initiated by Kerrigan (24) who employed capryl alcohol with an aqueous hydrofluoric acid solution of the oxides. Recently

Foos and Wilhelm (25) thoroughly reviewed the literature concerning the separation of tantalum and niobium and greatly extended the investigation of the liquid-liquid extraction process as a means for their separation. Included in their study were considerable data on a number of organic solvents which could be used in the preferential extraction of tantalum from an aqueous hydrofluoric acid solution.

Other investigators have also reported on liquid-liquid extraction of tantalum and niobium. In one report (26) the extractions were made on aqueous hydrofluoric-hydrochloric acid solutions with aliphatic and aromatic ketones, the distributions favoring the extraction of tantalum. Continuous countercurrent flow of a system employing hydrofluoric acid, hydrochloric acid and hexone in a twelve-foot, perforated-plate pulse column yielded fair purity of the separated oxides.

Werning and Higbe (27) used 12 normal hydrochloric acid for the preferential extraction of tantalum from mixed aliphatic and aromatic ketone solutions containing anhydrous tantalum and niobium pentachlorides. They obtained relatively pure oxides by using the system isobutyl ketone-diisobutyl ketone-12 normal hydrochloric acid. Presence of ferric chloride enhanced the extraction of tantalum to the aqueous hydrochloric acid phase.

Ellenburg, Leddicotte and Moore (28) quantitatively separated niobium and tantalum by liquid-liquid extraction of their hydrochloric acid solution with long-chain aliphatic and aromatic amines in organic solvents. Additional results indicated that sulfate and oxalate complexes of tantalum and niobium extract with the solvated amines. For tribenzylamine in methylene chloride, the niobium sulfate complex was quantitatively separated from that of tantalum when a ratio of fifteen to one was maintained between the volumes of organic and aqueous media, respectively.

Cabell and Milner (29) report a method of separation using anion exchange chromatography. A solution of tantalum and niobium in 3 molar hydrofluoric acid is put on a column of Deacidite FF, and niobium is then eluted with an aqueous solution of 3 molar hydrochloric acid and 0.1 molar hydrofluoric acid. Tantalum is recovered by elution with an aqueous solution of 4 molar ammonium chloride and 1 molar ammonium fluoride.

III. EXPERIMENTAL DETAILS AND RESULTS

A. Materials and Equipment

Materials

1. Ore concentrates from Argentina, South Dakota, and Africa.
2. Sodium Hydroxide, 76% flake, technical.
3. Potassium Hydroxide, 90% flake, technical.
4. Sodium Peroxide, Reagent.
5. Sulfuric acid, C. P., concentrated acid of sp. gr. 1.84.
6. Nitric acid, C. P., concentrated acid of sp. gr. 1.42.
7. Hydrochloric acid, C. P., concentrated acid of sp. gr. 1.19.
8. Hydrofluoric acid, 70% aqueous solution, commercial.
9. Cyclohexone, Eastman Org. Chem. Dist. Prod.
10. Dibutyl ether, technical.
11. Diethyl ketone, Carbide and Carbon Chem. Div.
12. Diisobutyl ketone, Eastman Org. Chem. Dist. Prod.
13. Methyl isobutyl ketone, technical.
14. Tributyl phosphate, Commercial Solvents Corp.
15. Iron powder, Reagent.
16. Zinc powder, Reagent.
17. Sodium Nitrate, technical.
18. Potassium Nitrate, technical.

Equipment

1. Variety of polyethylene containers.
2. Polyethylene funnel fitted with a short piece of tygon tubing and pinch clamp.
3. Empty polyethylene hydrofluoric acid bottles.
4. Iron crucible formed out of a pipe cap.
5. Iron crucible, 6" diameter and 40" high, formed by welding sheet into a cylinder.
6. Cement mixer.
7. Small rotary suction filter.
8. Large porcelain containers.
9. Muffle furnace.
10. Drying oven.
11. Other laboratory equipment.

B. Preliminary Experimentation

Each of the above processes for opening niobium and tantalum ores has certain limitations with regard to large scale operations. These limitations lend encouragement to studies for the development of a more favorable process. The purification and separation processes reported also leave much to be desired for efficient and economical operation in the large scale production of pure niobium and tantalum oxides.

In initiating research for a more favorable process for obtaining niobium and tantalum from their ores, a number of exploratory tests were made. One approach was a sulfuric acid treatment of ore concentrates at various temperatures. A molten salt bath consisting of 45 per cent sodium nitrate and 55 per cent potassium nitrate was used to immerse a round bottom flask containing the reaction mixture. Concentrated sulfuric acid was mixed with the finely ground ore concentrates in the flask and stirred

while heating. The reaction usually required an hour to an hour and a half of heating time. After the reaction had apparently subsided and the product set up to a stiff cake, the flask was taken out of the salt bath. The mass was removed from the flask with the aid of water. More water was added to precipitate any tantalum and niobium which may have dissolved and the solution was then filtered. The hydrofluoric-acid-soluble part of the residue was dissolved and filtered leaving the unreacted ore which was recovered and weighed. Table 1 gives results obtained by sulfuric acid treatment of the Argentine ore. The table shows that temperatures of about 300 degrees Centigrade are necessary for appreciable reaction.

Table 1

Effect of Temperature on Reaction of Sulfuric Acid on Ore.

Grams of ore	Milliliters of acid	Temperature (°C.)	Per cent reaction
50	50	237	50
50	50	250	56
50	50	275	59
50	50	295	68
50	75	300	69

A number of unreacted ore residues were combined to give a sample which was treated again with fresh concentrated sulfuric acid. The reaction of this unreacted ore sample was about equal to that of the original ore. In view of this observation it appears that, under proper conditions and with retreatment of the unreacted ore, the reaction might be made to go essentially to completion. Sulfuric acid has a decomposition temperature of about 330 degrees Centigrade but it fumes considerably below 300 degrees Centigrade. The loss of sulfuric acid by fuming possibly was a factor in the inefficiency and slowness of the reaction. As the reaction progresses the volume of the reacted ore is much greater than that of the unreacted ore and reaction products tend to envelop the residual ore. A process based on the sulfuric acid treatment might be developed but no further effort was made in that direction in the work reported here.

Another possible ore treatment method explored was the fusion with potassium hydroxide. The ore concentrate was placed on top of an equal weight of potassium hydroxide in an iron crucible and heated until fusion had taken place. A nearly complete reaction was obtained when the fusion was carried out in a furnace maintained at 500 degrees Centigrade. Since the potassium salts of niobium and tantalum are quite soluble in water, the fused material was treated with water. The solution was boiled to precipitate manganese dioxide and filtered to remove this and other insolubles. Difficulty was encountered at this point as only about 70 per cent of the tantalum and niobium dissolved by addition of water. Several procedures such as varying the amount of potassium hydroxide used in the fusion and repeated washing of the fused product with a potassium hydroxide solution were tried without success in attempts to dissolve all of the tantalum and niobium. If all of the tantalum and niobium had dissolved, they could have been easily precipitated as a mixture of sodium niobate and tantalate quite free of impurities by the addition of sodium hydroxide or sodium chloride. The insoluble portion complicated this possible procedure. There was no apparent method for easy and economical separation of the tantalum and niobium from the potassium hydroxide treatment.

The sodium hydroxide fusion method for the opening of the ore concentrates as previously carried out at this Laboratory (23) was extended. A satisfactory fusion was obtained with only one part of sodium peroxide and eleven parts of sodium hydroxide to ten parts of a South Dakota ore concentrate. This would represent considerable savings over the earlier method in which four parts of sodium peroxide were used to ten parts of ore. This satisfactory fusion then warranted further investigation of the sodium hydroxide process. Also in this process an improved treatment was desired to replace the repeated washing and leaching of the fusion product. These operations were slow and tedious and also could allow some loss of tantalum and niobium, which are slightly soluble.

In the absence of a better means of removing the impurities than by repeated washing and leaching, twenty pounds of the same South Dakota ore was treated in a batch fusion. Two pounds of sodium peroxide and 22 pounds of sodium hydroxide were employed. The reacted product was repeatedly leached with sodium hydroxide and nitric acid solutions and filtered in an attempt to obtain purification of the tantalic and

niobic acids. The washed residue of mixed oxides was then dissolved in 70 per cent hydrofluoric acid to yield about 12 liters of an aqueous solution containing about 500 grams of the combined oxides per liter of solution.

Portions of this hydrofluoric acid solution were used for some exploratory tests on possible means for obtaining pure tantalum and niobium. Concentrated sulfuric acid was added to a sample of this hydrofluoric acid solution and the solution was allowed to cool. Diethyl ketone was added. The solutions were shaken together and upon settling two phases were formed. The phases were separated and the small aqueous phase was precipitated with ammonium hydroxide and filtered. This precipitate was dried, ignited, calcined at 600-700 degrees Centigrade, and weighed. The color of this calcined precipitate was almost black, indicating a relatively large amount of impurities. The organic phase containing most of the tantalum and niobium was then washed with successive portions of an aqueous sulfuric acid solution. Each aqueous phase resulting from these washes and the remaining organic phase were precipitated with excess ammonium hydroxide and filtered. The precipitate, which in each case was white, was dried, ignited, calcined, and weighed. Qualitative analyses obtained by spectrographic means on each calcined precipitate indicated that the major part of the material that was back-washed by the portions of aqueous sulfuric acid consisted of niobium and the remaining organic phase was mostly tantalum.

Quantitative spectrographic analysis showed this residual tantalum oxide to contain only 0.23 per cent niobium oxide and the major portion of the niobium oxide extracted to contain only 1.8 per cent tantalum oxide. The original hydrofluoric acid solution contained these two oxides in a ratio of about two to one.

These data indicated that a process based on the transfer of both tantalum and niobium to an organic phase with back-extraction of niobium from this organic solution might be a satisfactory means of separating the niobium and tantalum. In addition the experiment indicated that most of the impurities not removed by the primary leaching of the sodium hydroxide fusion product could possibly be readily eliminated by this step in which both niobium and tantalum are transferred to the organic phase. This possibility of removing impurities further suggested that the primary leaching process

did not have to be very extensive. Such a process for opening the ore with a subsequent organic extraction has been developed and appears very favorable on the basis of cost of high purity products.

C. Opening of Niobium and Tantalum Ores

In the method presented here the ore is fused with sodium hydroxide and partially leached with water and then with sulfuric acid solution to obtain the acid oxides in a hydrofluoric acid soluble residue. Conditions were developed for a satisfactory fusion for an Argentine ore. A series of tests was run using charges consisting of 30 grams of Argentine ore plus 31 grams of sodium hydroxide which were heated for 20 minutes at various temperatures. The results are given in Table 2. The per cent of reaction was determined from the weight of unreacted ore remaining after the fusion. The fused material was separated from the unreacted ore by treating the fused product with hydrofluoric acid and decanting the liquid phase.

Table 2

Comparison of the Per Cent of Argentine Ore Which Had Reacted at Various Temperatures.

Temperature (°C.)	Per Cent Reaction
400	66
475	86
500	90.5
550	95
600	96
650	97.3
700	98.4
750	98.3

The results indicate that above 550 degrees Centigrade nearly complete reaction of the ore can be obtained. The value did not approach 100 per cent at any temperature due to some large particles in the ore. The Argentine ore was

ground by passing it through a jaw crusher and micro-pulverizer hammer mill. A sieve analysis showed that 78 per cent of the ore passed through a 200 mesh sieve. One fusion was carried out at 600 degrees Centigrade using ore that passed through the 200 mesh sieve. Only 0.3 per cent did not react in this fusion; therefore, it is assumed that essentially complete reaction of the ore can be obtained at 600 degrees Centigrade if all of it is ground to 200 mesh.

A series of fusions was made using 20 grams of ore with various amounts of sodium hydroxide. When 12 grams of sodium hydroxide was employed, the reaction was about three-fourths complete. Nearly complete reaction was obtained with a fusion mixture of 16 grams of sodium hydroxide and 20 grams of ore. The decision as to amount of sodium hydroxide to use in a particular fusion also depended on the treatment of the fused product. From previous work (30) it had been shown that the sodium salts of niobic and tantalic acids were somewhat soluble in water or in a basic solution which is less than 1 normal sodium hydroxide. Therefore, sufficient extra sodium hydroxide was added to the fusion mixture to assure a 1 normal sodium hydroxide solution when the fused product was treated with water for subsequent washing. This excess of sodium hydroxide not only insured a basic wash solution of at least 1 normal sodium hydroxide but also aided in obtaining a more nearly complete fusion of the ore.

This basic wash of the fused product removed considerable silicon, tin, aluminum, manganese, and sodium. This wash was dark green in color, indicating the presence of sodium manganate. When manganese is fused with excess sodium hydroxide in the presence of air, part, but never all, of the manganese is converted to sodium manganate (VI) which is soluble in sodium hydroxide solution (31). The equilibrium reaction of sodium manganate with water is as follows:

$$3Na_2MnO_4 + 2H_2O \rightleftharpoons 2NaMnO_4 + 4NaOH + MnO_2.$$

Basic conditions tend to shift this equilibrium to the left while heat and non-basic conditions tend to shift it to the right and precipitate manganese dioxide. Therefore, in treating the fused product, it was cooled before adding the water and stirring in order to obtain more of the manganese in the soluble form. However, there is usually much manganese that is in the insoluble form and must be removed with the iron and other impurities by further treatment.

In most of the earlier work nitric and hydrochloric acids were effectively employed for the further treatment of the residue remaining after the basic leach of the fused product. Iron and manganese were dissolved and a white residue of the earth acids was obtained with either nitric or hydrochloric acids. Since a process acceptable for large scale production is being considered, an attempt was made to replace the more costly nitric and hydrochloric acids by sulfuric acid. In order to study the effect of sulfuric acid on the treatment of the residue, various concentrations of sulfuric acid were added to portions of the basic insoluble residue. There was evidence of reaction as the brown residue turned to a reddish color after sulfuric acid was added, but the white residue characteristic of the purified niobic and tantalic acids was not obtained. Small amounts of several reagents such as hydrogen peroxide, hydrochloric acid, nitric acid, and zinc powder were then added to the above sulfuric acid solutions in order to cause the desired reaction. While one of the plain sulfuric acid solutions was being stirred, some metallic iron powder was added. A sudden change of color to white was observed, indicating that most of the original iron and manganese compounds had dissolved. Evidently the reducing action of the iron powder was effective in bringing about this solution in sulfuric acid.

Since niobic and tantalic acids are soluble to a small extent in the more concentrated sulfuric acid solutions required to dissolve the manganese, water was added to dilute the sulfuric acid to about 1 molar. Boiling of this solution was found necessary in order to destroy the colloidal form of the niobic and tantalic acids. Filtration gave a yellow colored filtrate and a nearly white residue of tantalum, niobium and some impurities.

The white residue was dried to constant weight at a temperature of 165-200 degrees Centigrade in order to determine the total amount of oxides present. This dried residue dissolved readily in 70 per cent hydrofluoric acid to give a solution with a low water content. If this dried residue is calcined at 600-700 degrees Centigrade, it loses about 20 per cent of its weight, but the calcined residue is difficult to dissolve in hydrofluoric acid solution.

A laboratory scale procedure based on the earlier experiments was more or less adopted as standard for a series

of tests on opening the ores. On this laboratory scale, 30 grams of the finely ground ore is placed on top of 31 grams of sodium hydroxide in an iron crucible. The mixture is heated and when the sodium hydroxide melts it is thoroughly stirred in the presence of air until the mass thickens. This product is heated further at 600 to 650 degrees Centigrade for 20 to 30 minutes. The resulting reacted mixture is cooled and washed with 200 milliliters of cold water and the solution is filtered. The residue, which may be red-brown in color, is made into a slurry by adding some water and stirring. Stirring is continued while fifty milliliters of dilute sulfuric acid (1:1) and about one gram of powdered iron are added. After the reaction has subsided the mixture is diluted to 600 milliliters with water and heated to boiling. The insoluble residue, which contains the niobic and tantalic acids, is recovered by filtration or decantation. It is washed and dried at about 200 degrees Centigrade to give a mixture of niobium and tantalum oxides with generally five to ten per cent impurities, depending on the ore composition.

In order to determine its degree of versatility, the above procedure was applied to ore concentrates from a number of sources. These various ore concentrates are listed in Table 3. The percentage of earth oxides is an approximation of the total earth oxides in the individual

Table 3

Proportion of Tantalum and Niobium in the Various Ores.

Source	Per cent earth oxides	Per cent Ta_2O_5	Per cent Nb_2O_5
Argentina	69	22.5	77.5
South Dakota #1	75	53	47
South Dakota #2	60	37	63
South Dakota #3	63	29.5	69.5
South Dakota #4	70	44	66
Nigeria	69	8.5	91.5
Africa	67	25	75

ores. The approximation was made from the weight of the mixture of leached oxides of tantalum and niobium recovered by the above chemical treatment of the ore concentrates. These values are only roughly indicative since impurities such as titanium dioxide actually were present. Each oxide mixture was analyzed by X-ray fluorescence (32) to give its relative amounts of Ta_2O_5 and Nb_2O_5. These analytical data represent only the values for each oxide with respect to the amounts of both in the impure mixture.

The fusion of these ores with sodium hydroxide yielded a granular product with a small amount of unreacted ore. The color of the various fused products varied from a yellow-green to a very dark green. The amount of iron powder needed in the sulfuric acid leach to remove most of the dark color from the residue and leave nearly white niobic and tantalic acids after filtration varied with the amount of manganese in the particular ore. A review of the qualitative analytical results on the materials carried in solution by the basic wash and by the sulfuric acid-iron treatment indicated successful washing and leaching. In two cases, however, a small amount of tantalum and niobium was found in the basic extract; this small loss could have possibly been avoided by the use of a slightly larger proportion of sodium hydroxide in the fusion.

D. Separation of the Tantalum and Niobium

In the ore treatment, the objective was to open the columbite-tantalite ore concentrate, remove a majority of the impurities with the minimum loss of tantalum and niobium, and prepare a residue of the oxides which is readily soluble in an aqueous 70 per cent hydrofluoric acid. This objective was set to accomodate a possible purification-separation procedure based on the use of hydrofluoric acid solution in liquid-liquid extraction. In subsequent experiments on hydrofluoric acid-sulfuric acid solutions of this residue it was found that the niobium and tantalum could be almost quantitatively extracted by an organic phase, leaving most of the impurities behind. Further, it was found that the niobium could be preferentially back-extracted into a sulfuric acid solution from the organic solution, leaving tantalum of high purity.

The data on the extraction in the preliminary work with the hydrofluoric acid-sulfuric acid-diethyl ketone system suggested that such a procedure might be practical for the separation of tantalum, niobium, and impurities.

The diethyl ketone, however, is quite soluble in the aqueous phase and it is also more costly than some other less soluble organics that might serve the purpose equally well. Reference was made to a table in which extraction data on niobium and tantalum are given for a number of organics (25) in order to select a substitute for the diethyl ketone. After considering extractability, availability, cost, and the solubility in water, cyclohexone, diisobutyl ketone, methyl isobutyl ketone (hexone), and tributyl phosphate were selected for test extractions. It was found that the cyclohexone was decomposed to some extent on contact with strong sulfuric acid and it was therefore not tested further. Diisobutyl ketone readily extracted the tantalum and niobium with very little impurities but on the back-wash treatment there was not the degree of separation desired for niobium and tantalum. Tributyl phosphate has a high extractability but has the disadvantage that its density is very nearly the same as the hydrofluoric acid solution. This density problem may be overcome to a certain extent by diluting the tributyl phosphate with a less dense solvent such as dibutyl ether. Preliminary tests indicated that hexone may be a good substitute for diethyl ketone.

One problem encountered when either hexone or tributyl phosphate was used instead of diethyl ketone was that the small amount of impurities which are carried along with tantalum and niobium by the organic phase in the primary extraction could not be cleanly back-washed. That is, the 6 molar sulfuric acid used to back-wash the impurities also extracted a lot of tantalum and niobium from the organic phase. Hydrochloric acid was substituted for sulfuric acid, but then very little iron was washed away from the organic phase. An effort was made then to find some way to prevent a carry-over of the impurities into the organic phase. Two factors were found to limit the transfer of impurities with tantalum and niobium to the organic phase. First, the organic was added directly to a hydrofluoric acid solution of the oxides rather than to a hydrofluoric-sulfuric acid solution as was done in the preliminary work. Second, the hydrofluoric acid was maintained at the minimum necessary to dissolve the residue of oxides, because some impurities were extracted by the organic when the hydrofluoric acid content was high.

By the procedure given in the previous section, 450 grams of Argentine ore was processed and yielded 455 grams of dried residue rich in the oxides. Twenty grams of this dried residue readily dissolved, except for the unreacted ore portion, in 20 milliliters of 70 per cent hydrofluoric acid. Twenty-five grams of the residue when treated similarly, left in addition

a very small amount of undissolved earth oxides. It was assumed then that 20 milliliters of 70 per cent hydrofluoric acid was about the minimum amount of this acid required to dissolve 25 grams of the dried residue. Hydrofluoric acid solutions of the dried residue were then prepared in this manner for extraction tests with hexone and with tributyl phosphate.

A solution of 25 grams of the dried residue was dissolved, as described, in a polyethylene container. Twenty-five milliliters of hexone was added and the two liquids were mixed by shaking them for about two minutes. The phases were allowed to separate and the aqueous phase was shaken a second time with 25 milliliters of hexone. The two portions of the organic phase were then combined for studies on the separation of the tantalum and niobium. Further extraction of the resulting aqueous phase indicated about 0.64 grams of tantalum and niobium oxide had not been extracted and that tantalum and niobium had been separated from about 1.95 grams of oxides of impurities. The combined organic phase was washed with 4 milliliters of aqueous 6-molar sulfuric acid and then successively washed with five 20-milliliter portions of aqueous 2 molar sulfuric acid.

Another 25 grams of dried residue was then dissolved in hydrofluoric acid and extracted in a similar manner with two portions of a solution of tributyl phosphate and dibutyl ether in a volume ratio of three to one, respectively. Forty milliliters and 25 milliliters were the volumes of this organic solution used in the first and second extractions, respectively. The total organic phase containing the tantalum and niobium was then washed with a 4-milliliter portion of 6 molar sulfuric acid and five 20-milliliter portions of 1 molar sulfuric acid.

Each aqueous phase and the remaining organic phase from both hexone and tributyl phosphate extractions were treated with excess ammonium hydroxide. The precipitates were recovered, dried, ignited, calcined at 600-700 degrees Centigrade, and weighed. The weight of oxide precipitated from each phase and the quantitative analysis of the oxide for tantalum and niobium are given in Table 4. The relative niobium and tantalum content was obtained by X-ray fluorescence (32) and spectrographic analysis. The first method was employed for mixtures containing between 4.0 and 98 per cent tantalum. Spectrographic methods were used for samples containing less than 4.0 per cent or more than 98 per cent tantalum.

Table 4

Data on Aqueous Sulfuric Acid Wash of Organic Solution.

Hexone

	4 ml. 6M H_2SO_4	20 ml. portions of 2M H_2SO_4 1	2	3	4	5	Residual organic phase
Sample #	P-1	P-2	P-3	P-4	P-5	P-6	P-7
Wt. oxide (g.)	.745	5.40	3.58	1.81	.55	.06	3.66
Wt. Ta_2O_5 (g.)	.057	.180	.093	.054	.077	.03(?)	3.65
% Nb_2O_5	-	-	-	-	-	-	.29
% Ta_2O_5	7.7	3.3	2.6	3.0	14.0	-	-

Tributyl Phosphate-Dibutyl Ether (3-1)

	4 ml. 6M H_2SO_4	20 ml. portions of 1M H_2SO_4 1	2	3	4	5	Residual organic phase
Sample #	P-8	P-9	P-10	P-11	P-12	P-13	P-14
Wt. oxide (g.)	.53	5.15	2.58	.96	.205	.04	4.13
Wt. Ta_2O_5 (g.)	.054	.110	.049	.026	.025	.02(?)	4.12
% Nb_2O_5	-	-	-	-	-	-	.14
% Ta_2O_5	10.3	2.15	1.9	2.7	12.5	-	-

The higher percentage of tantalum in the first wash is assumed to be due to the fact that the hydrofluoric acid concentration was the highest at this point of the washing treatment. There seems to be a tendency for less and less transfer of tantalum as the washing progresses. This is possibly due to a depletion of the hydrofluoric acid in the organic phase. The transfer of niobium decreases more rapidly because of the depletion of both niobium and hydrofluoric acid in the organic phase. As a result, the per cent of tantalum extracted by washing drops to a minimum at about the third wash by this procedure. A further check was made on the effect of the hydrofluoric acid by adding hydrofluoric acid to an organic (hexone) phase after the first 20-milliliter washing. The weight of the oxide in the second 20-milliliter wash was down to about one-third of the value shown for hexone in the table and the percentage of Ta_2O_5 had gone up to 21 per cent. The results of several similar hexone extractions of a hydrofluoric acid solution, in which only 20 grams of dried residue was dissolved in 20 milliliters of hydrofluoric acid, showed that with this excess of hydrofluoric acid the percentage of tantalum was higher in the first few washes.

These results in experiments with excess hydrofluoric acid indicate that under such conditions tantalum may form some complex or compound such as H_3TaF_8 that favors the aqueous phase and that under the same conditions niobium tends to form a compound that favors the organic phase. The niobium behavior possibly can be explained by an equilibrium expressed by this equation,

$H_2NbOF_5 + 2HF \rightleftharpoons H_2NbF_7 + H_2O$, in which the H_2NbOF_5 favors the aqueous phase and the H_2NbF_7 favors the organic phase. Likewise, the tantalum equilibrium might be $H_2TaF_7 + HF \rightleftharpoons H_3TaF_8$, in which the H_2TaF_7 favors the organic while the H_3TaF_8 favors the aqueous phase.

A summation of the total oxides recovered from the hexone gives a value of 15.9 grams, while from the tributyl phosphate-dibutyl ether solution only 13.6 grams were recovered. This would indicate that the tributyl phosphate-dibutyl ether extraction from the original aqueous hydrofluoric acid solution was not as effective as the hexone extraction. However, if the summations are made of the total tantalum oxide recovered from each organic, it is seen that 4.41 grams of Ta_2O_5 are recovered from the tributyl phosphate solution while only 4.15 grams of this oxide are recovered from the hexone phase. In the extraction from the

original aqueous hydrofluoric acid solution more tantalum was extracted by the tributyl phosphate-dibutyl ether solution than by the hexone. It is to be noted, however, that the quantity and purity of the tantalum remaining in the final organic exceed that for the hexone.

The qualitative spectrographic analyses of the samples of Table 4 are given in Table 5 and the spectral intensity of the various elements in each sample is indicated. The amount of silicon does not appear to diminish as the extraction progresses. It is assumed that the trace amount of silicon present is that which is picked up by calcining the precipitates in porcelain crucibles. It is to be noted that tin, silicon, and titanium are completely eliminated from tantalum and niobium by the extraction into either of the organics followed by the single back-wash with 6 molar sulfuric acid. This same treatment reduces iron and manganese to only trace amounts.

Table 5

Qualitative Analyses of the Samples of Table 4.

Sample #	Al	Fe	Mn	Mg	Nb	Si	Sn	Ti	Ta
P-1	T	S	S	FT	VS	M	T	T	M
P-2	T	M	T	-	VS	T	-	-	T
P-3	T	T	-	FT	VS	T	-	-	T
P-4	FT	T	T	-	VS	T	-	-	T
P-5	FT	T	T	-	VS	T	-	-	M
P-6	FT	T	FT	T	VS	T	-	-	S
P-7	-	T	T	-	T	T	-	-	VS
P-8	T	M	M	FT	VS	T	T	FT	M
P-9	T	T	T	-	VS	T	-	-	T
P-10	FT	FT	FT	FT	VS	T	-	-	T
P-11	FT	FT	-	-	VS	T	-	-	T
P-12	FT	T	T	-	VS	T	-	-	S
P-13	FT	FT	T	FT	VS	T	-	-	S
P-14	-	T	T	-	T	T	-	-	VS

- not detected
FT faint trace
T trace
M minor
S strong
VS major

Niobium oxide with less than 800 parts per million of tantalum oxide was obtained from an aqueous solution prepared by combining the first three 20-milliliter 2 molar sulfuric acid washes of a hexone extract similar to those of Table 4. This new aqueous phase was then scrubbed with one five-milliliter and then three successive ten-milliliter

washes of fresh organic solvent. The niobium recovered from the residual aqueous phase analyzed less than 800 parts per million of tantalum, the limit of the method of detection of tantalum in niobium. Both hexone and tributyl phosphate were used as the organic solvents for these scrubbing operations and similiar results were obtained in both cases.

Likewise, after washing a hexone extract four times with 20 millliliters of 2 molar sulfuric acid, 2.5 milliliters of 70 per cent hydrofluoric acid was added to the tantalum-rich hexone phases and five successive 20-milliliter, 2 molar sulfuric acid washes were made. The tantalum oxide which was precipitated from this final organic phase contained about 0.031 per cent niobium oxide.

A review of the separation of tantalum and niobium employing liquid-liquid extraction as given in this study points out that tantalum and niobium can be separated in fair purity by batchwise extraction. However, if the pure oxides are desired in quantity, a continuous countercurrent operation based on this system of extraction would be desirable for greater economy.

V. LITERATURE CITED

1. Hughes, D. J. and Harvey, J. H., "Neutron Cross Section", Report BNL-325, p. 11, Aug. 1955.

2. Friend, J. N., "A Text-Book of Inorganic Chemistry", Vol. 15, Part 3, p. 117-133, London, Charles Griffin and Company, Limited, 1929.

3. Berzelius, J. J., Ann. Chim. Phys., 3, 140 (1816).

4. Mellor, J. M., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 4, p. 837-925, New York, Longman, Green and Co., 1947.

5. Rose, H., Pogg. Ann., 113, 30 (1864).

6. Simpson, E. S., Chem. News, 99, 243 (1909).

7. Gibbs, O. W., Amer. Journ. Science, 37, 355 (1864).

8. Giles, W. B., Chem. News, 99, 1 (1909).

9. Joly, A., Ann. Ecole Norm., 6, 138 (1877).

10. Hahn, F. L. and Franke, W., German Patent D.R.P. 437,561 (1925).

11. Sears, G. W., J. Amer. Chem. Soc., 48, 343 (1926).

12. Rohiner, R., Compt. rend., 212, 614 (1941).

13. Bhattacharya, H., J. Indian Chem. Soc., 29, 871-9 (1952).

14. Balke, C. W., Ind. Eng. Chem., 21, 1002-7 (1929).

15. Placek, C. and Taylor, D. E., Ind. Eng. Chem., 48, 686 (1956).

16. Sears, G. W. and Williams, L. R., Atomic Energy Comm. Report U-19160, June 30, 1951.

17. Oka, Y. and Miyamota, M., J. Electrochem. Soc. Japan, 17, 63-6 (1949).

18. Meyers, R. H. and Greenwood, J. N., Proc. Australasian Inst. Mining and Met., 129, 41-53 (1953).

19. Fink, C. G. and Jenness, L. G., Am. Inst. Mining and Met. Eng., Tech. Pub. No. 379, 18pp. (1931).

20. Fowler, R. M., U. S. Patent 2,481,584 (Sept. 13, 1949).

21. Jenness, L. G., U. S. Patent 1,834,662 (Dec. 1, 1932).

22. Cavelliez, F., U. S. Patent 2,429,671 (Oct. 28, 1947).

23. Wilhelm, H. A., Unpublished Report, Atomic Energy Comm. Report ISC-290, p. 23, Sept. 20, 1952.

24. Kerrigan , J. V., Unpublished Research, Ames Laboratory, Iowa State College, 1952.

25. Foos, R. A. and Wilhelm, H. A., "Application of Liquid-Liquid Extraction for Separation of Tantalum and Niobium", Atomic Energy Comm. Report ISC-694, Aug. 1954.

26. Werning, J. R., Higbe, K. B., Grace, J. T., Speece, B. F. and Gilbert, H. L., Ind. Eng. Chem., 46, 644-52 (1954).

27. Werning, J. R. and Higbe, K. B., Ind. Eng. Chem., 46, 2491-8 (1954).

28. Ellenburg, J. Y., Leddicotte, G. W. and Moore, F. J., Anal. Chem., 26, 1045 (1954).

29. Cabell, S. and Milner, G. W., Anal. Chim. Acta, 13, 258-67 (1955).

30. Murray, E., Unpublished Research, Ames Laboratory, Iowa State College, 1954.

31. Sidgewick, N. V., "Chemical Elements and Their Compounds", Vol. 2, p. 127, Oxford, Clarendon Press, 1950.

32. Campbell, W. J. and Carl, H. F., Anal. Chem., 26, 800 (1954).